Biomimicked Polymer Surfaces Exhibiting Superhydrophobic and Anti-reflective Properties

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A Dissertation Submitted to
Indian Institute of Technology Hyderabad
In Partial Fulfilment of the Requirements for
The Degree of Master of Technology

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

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June, 2013

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Approval Sheet

This thesis entitled "Biomimicked polymer surfaces exhibiting superhydrophobic and antireflective properties" by Srinadh Mattaparthi is approved for the degree of Master of Technology from IIT Hyderabad.

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Abstract

Materials, objects and processes found in nature functions from macro-scale to the nano-scale. Bio-inspiration or biomimetics is a tool to mimic these natural objects to develop functional materials which provide desired properties. There are a large number of examples found in nature such as plants, bacteria, land animals, aquatic animals and insects which provide an inspiration to mimic some structural and functional properties owned by them. For example some plant leaves and flower petals like lotus leaf, rice leaf, taro leaf and rose petal are well known for their superhydrophobic and self-cleaning properties due to the multiscale structural patterns present on their surfaces. This self-cleaning phenomenon also known as "Lotus effect" is due to high contact angle and low contact angle hysteresis.

India canna is a common garden plant however structural properties of its various parts such as petal, leaf and seedpod have not been studied in literature. In this work, we studied the super hydrophobic nature of India canna plant. In case of seedpod, it is the high aspect ratio multiscale structures that cause the superhydrophobicity however interestingly in case of leaf and petal, it is low aspect ratio bump like structures for similar behaviour. We mimicked these structural patterns into a number of polymers like PDMS and an organic (resorcinol formaldehyde) gel and found that these biomimicked polymer surfaces also exhibit superhydrophobic property. To add the novelty, polymer surfaces with these multiscale surface patterns has also been studied for their antireflective properties with an inspiration from the moth eye structure. The facile fabrication of superhydrophobic as well as antireflective polymer surfaces by a low cost and simple biomimicking route opens the possibilities of using such surfaces for a wide variety of engineering applications including energy storage devices.

DEDICATION

Dedicated to my parents, my teachers, and my friends

Acknowledgments

First I would like to thank my supervisor **Dr. Chandra Shekhar Sharma** for his support and guidance throughout this work.

I would also like to thank the committee members **Dr. Saptarshi Majumdar, Dr. Debaprasad Shee, Dr. Prem Pal** for their time and suggestions.

Furthermore, I would like to thank Ms. Anulekha for SEM image analysis, Mr. Tamal and Mr. Prakash for contact angle measurement and Mr. Sudarshan helping for confocal microscopic images.

Finally I would like to thank Mr. Manohar, Mr Lokesh, Mr. Harsha, Ms. Akansha, Ms. Ramya, Mr. Suresh, Mr. Tejesh, Ms. Lakshmi and Mr. Rajendar for teaching various protocols used in this experimental work and my friends.

Nomenclature

ARC	Antireflective coatings
AOI	Angle of incidence
CA	Contact angle
CVD	Chemical vapour deposition
PDMS	Polydimethylsiloxane
RF	Resorcinol Formaldehyde
SEM	Scanning Electron Microscope
SWS	Sub-wavelength structures
UV	Ultra violet
VIS	Visible
r	Reflection
n	Refractive index
%R	Percentage of reflection
%T	Percentage of transmission
γ	Interfacial free energy
γ_{SV}	Interfacial free energies at solid and vapour
γ_{SL}	Interfacial free energies at solid and liquid
γ_{LV}	Interfacial free energies at liquid and vapour
nm	nanometer
µm	micrometer
mm	millimeter
gm	grams

Contents

Chapter 1

Introduction

1.1 Biomimetics

Biomimetics (or) Bioinspiration is a highly interdisciplinary field involving understanding of biological functions and mechanisms of different organisms in nature and applying them in day today life. It is derived from the Greek word Biomimesis [1]. The word was coined by polymath Otto Schmitt in 1957. Later a woman named Janine M. Benyus in 1997, created a subject called Biomimicry [2]. It is a subject that combines both engineering and biology. The word biomimicry is composed of two words, bio (means life) and mimicry (means to imitate). The reason for biomimicry is to look into nature as a model and mimick them to create a sustainable solution of human problems. Nature's materials, designs and functions have always been inspiring humans since long time. Some interesting examples which were mimicked by man include aircrafts by observing birds flying; fencing consists of thorns by some plants having thorns on their stems and Velcro by cockleburs (Figure 1.1(a) which has hook like structures on the burs which sticks to fabrics. Recently due to the emergence of nanotechnology, nanostructure mimicking from nature has also gained importance.

Most of the nature objects, materials function on the macroscale to the nanoscale. Mimicking those functions and process found in nature, one can fabricate the functional surfaces. Some interesting examples are shown in Figure 1.1. As similar to Nambi desert beetle wings (Figure 1.1 (d)) which shows both hydrophobic and hydrophilic nature has also been biomimicked for its use as water harvester [3]. Gecko foot (Figure 1.1 (f)) has micro/nanoscale high aspect ratio beta keratin structures can be used as reusable adhesives [4]. Whale on their flippers (Figure 1.1 (b)) has bump like structures called tubercles, which results in a better control as the bumps make it easier for the whale to slit the water as it swims and turns. Mimicking these tubercles can be used wind turbine blades [5].

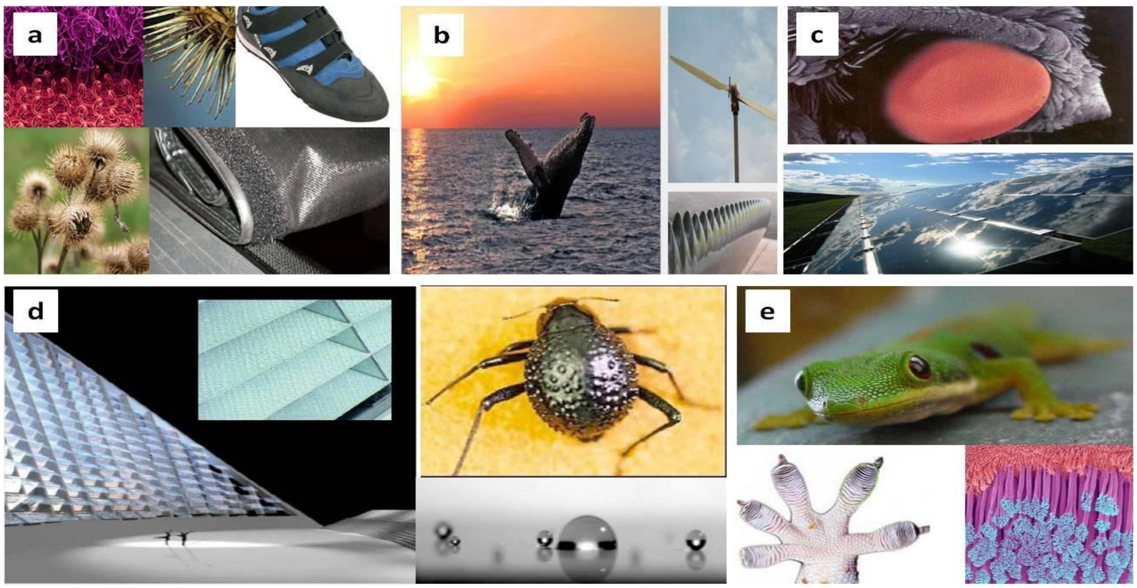

Figure 1.1: Bioinspiration examples (a) Velcro inspired from Cocklebururs [6], (b) Wind turbines inspired from whale flippers [7], (c) Anti-reflective surfaces inspired from moth-eye [8], (d) Water harvester inspired from nimbi desert beetle insect [9], and (e) Re-adhesive tape inspired from Gecko feet [10].

1.2 Superhydrophobic surfaces:

The concept of superhydrophobicity was first inspired from lotus leaf in nature. Due to their self cleaning behaviour, the lotus leaf is referred as “lotus effect” [11]. Wettability factor is one of the most important properties of liquid in contact to a solid surface. The contact angle is primarily used to characterize the surface wettability. The liquid contact angle on the solid flat surface can be correlated to three interfacial free energies, free energies at the solid-air (γ_{SV}), solid-liquid (γ_{SL}) and liquid-air (γ_{LV}) interfaces, by the Young‘s equation:

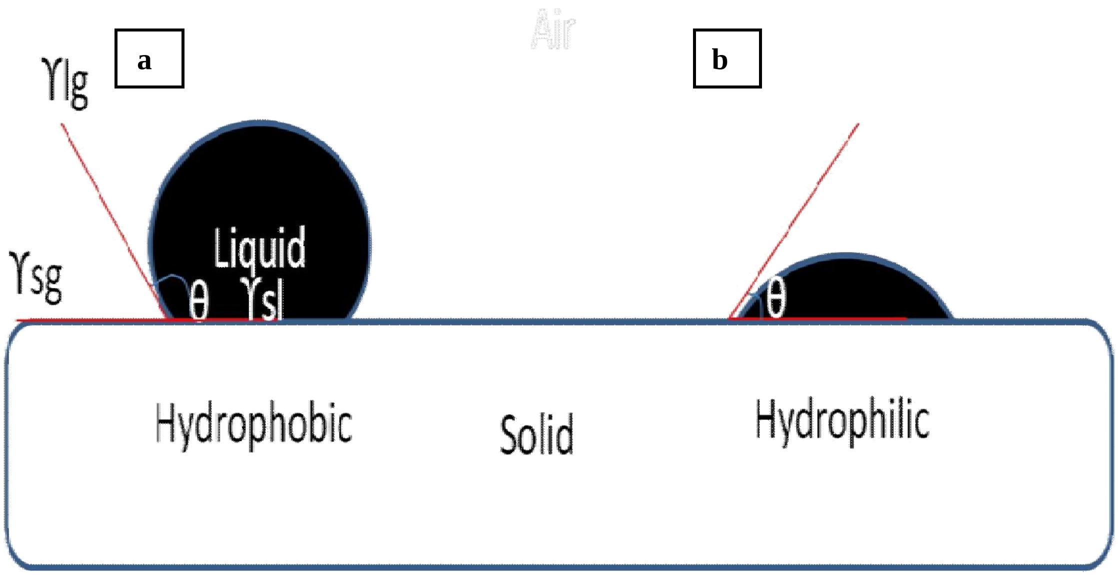

Figure 1.2: Contact angle of liquid drop on a flat solid surface (a) Hydrophobic surface (b) Hydrophilic surface.

Surface which attracts water are termed as hydrophilic and contact angle for these surfaces is less than 90° as shown in Figure 1.2 (b). Whereas the surfaces which repel water are termed as hydrophobic and contact angle in this case is greater than 90° as shown in Figure 1.2 (a). Superhydrophobic surfaces are generally described with water contact angle greater than 150°.

The study of superhydrophobic surfaces have been started as early as the 1940's, however there is a growing interest in the fabrication of superhydrophobic surfaces in last decade due to their wide variety of applications such as self-cleaning coatings [12,13], anti-sticking [14,15] and anti-contamination [16,17]. A number of attempts have been done to create artificial super hydrophobic surfaces by using various techniques such as electrospinning

[18], chemical vapour deposition(CVD) [19], plasma etching [20], sol-gel processing [21], chemical deposition and chemical etching [22]. As all these methods are either expensive or time consuming, Biomimicking is still considered to be simple and robust method.

Biomimicking has also been studied in detail for the fabrication of superhydrophobic surfaces. Some of the examples to mimic the natural surfaces are lotus leaf as shown in the Figure 1.3(a), rice leaf (Figure 1.3 (b)), rose petals (Figure 1.3 (c)) and water striders (Figure 1.3 (d)) [23]. In most of these cases, superhydrophic behaviour is due to a unique arrangement of low-aspect ratio micro and nano-structures on the surfaces and their applications were shown in the Figure 1.3 (e).

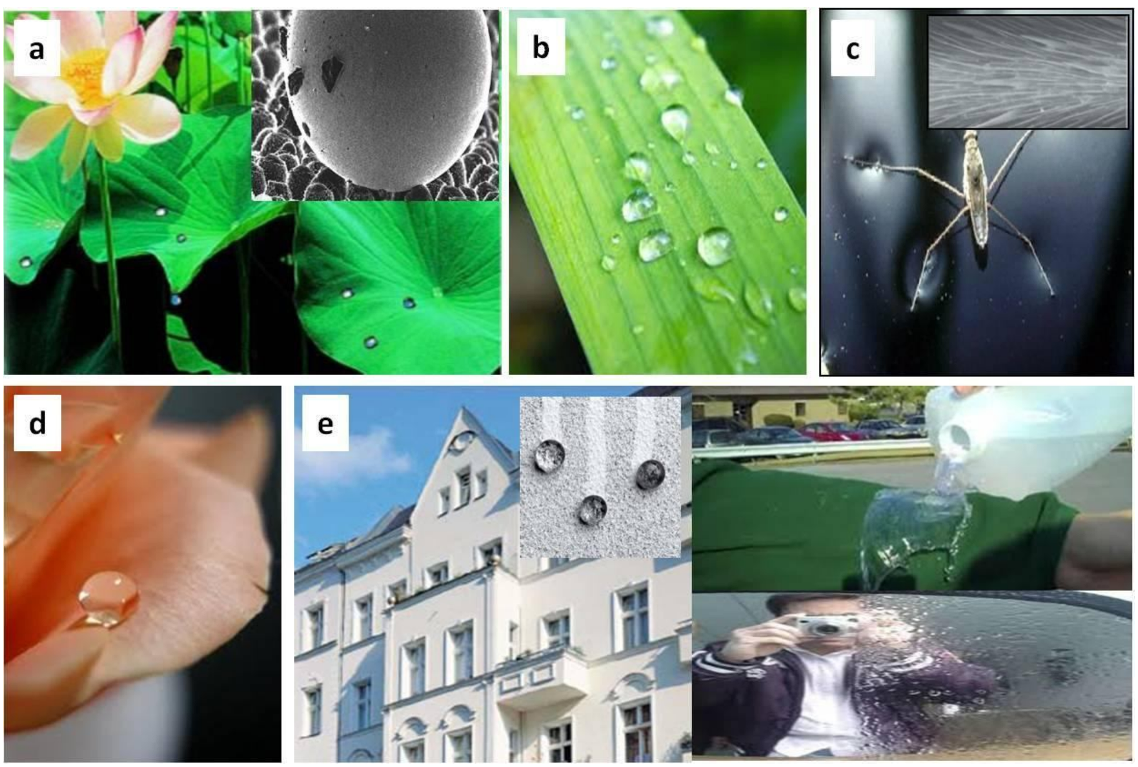

Figure 1.3: Superhydrophobic surfaces from nature. (a) Lotus leaf [9], (b) Rice leaf [24], (c) Water strider [25], (d) Rose petal [26], (e) Superhydrophobic surfaces applications like self cleaning textiles, paints and glass [9].

1.3 Antireflective surfaces:

Antireflective surfaces are widely used in variety of applications like car dashboards, computer screens and most importantly for solar cells. Antireflection can be achieved by antireflective coatings. Normally reflective surfaces have high refractive index relative to surrounding medium (air), which results in high reflectivity. So, the more the refractive index the more the reflection occurs. Reflection(r) can be easily calculated by using Fresnel equation [27] which is at normal angle of incidence (AOI) between two mediums of refractive indices n1 and n2.

$$r = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2$$

The above equation describes that the larger the difference in refractive indices between the two medium, the greater the portion of the light will be reflected.

Reflection can be suppressed by using antireflective coatings. The most common antireflective coating technology in use today is thin film anti reflective coatings. These thin film anti-reflective coatings can be divided into single layer antireflective coatings and multilayer antireflective coatings [28]. But these antireflective coatings are limited up to some extents like, radiation damage, adhesion problems and cannot be used for broad range of incident light.

1.4 Role of roughness in antireflective surfaces:

Taking inspiration from nature, certain species of moth on their corneal surfaces has arrays of nanostructures will act as antireflective properties shown in the Figure 1.1 (c). Incident light cannot resolve the individual features of these moth-eye arrays and so the patterns exhibit like effective refractive index ratio between corneal to air. The features are shaped in such a way that this refractive index ratio gradually increases from air into the cornea and also the open space between the features on the surface has the potential to collect air. The probability of collecting air will be more in between nanobump which also leads to a gradual increase in effective refractive index. So this eliminates the discontinuity in refractive index at the interface and minimises reflection [29] as shown in the Figure 1.4 (b). Apart from the moth eye structures, some plant petals having convex epidermal cells of few micrometer heights on their surfaces also show antireflective properties. The reduction of reflection on these surfaces is caused by multiple reflections between the convexly shaped epidermal cells [30] and also by path lengthening effect caused by micro papillae on petal surfaces [31] as shown in the Figure 1.4 (b). In Figure 1.4, when incident light strikes the both patterned surface (Figure 1.4 (b)) and plain surface (Figure 1.4 (a)), we can observe that patterned surfaces show zero reflection than the plain surface. So any roughening of the surface reduces reflection by increasing the chance of reflected light bouncing back onto the surface, rather than out to the surrounding air [32]. This can be done by surface texturing or creating micro/nanostructures as shown in Figure 1.4. The fabrication of such micro/nanostructures on required material could be more effective than thin film anti reflective coatings, which can be used in solar cells, computer screens.

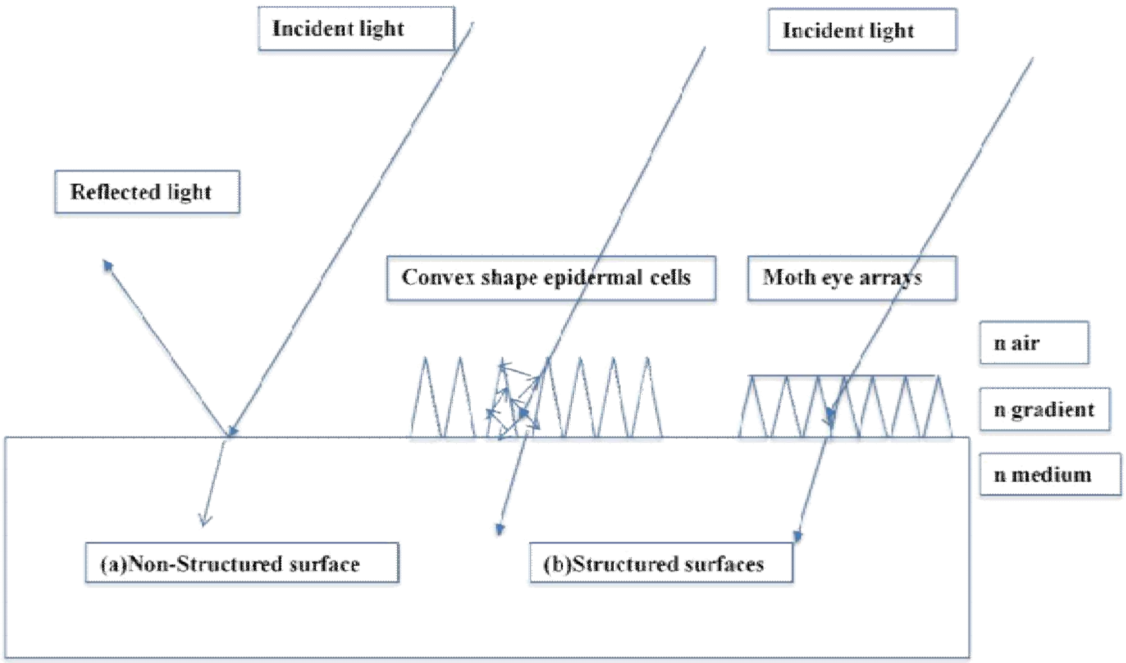

Figure 1.4: Left side (a) shows when incident light strikes the normal plain surface, some part of the light is entering into the surface (medium) and some part of light is reflecting. Right side (b) shows when incident light strikes the surface having convex shape epidermal cells, there occurs multiple reflections between the convex shape cells as well as path lengthening effect on individual convex shape epidermal cell and also when incident light strikes moth eye arrays like structures, all the light was trapped between the bumps and entering into the surface (medium).

Chapter 2

Materials and Methods

2.1 Indian canna: An example to inspire this work

In this work, we report bio-mimicking of Indian canna seedpod which is also known as Canna Indica, belonging to Cannaceae family, a native of the Caribbean and tropical America. It is also been widely cultivated as a garden plant as shown in Figure 2.1 (a). Here we have used the plant seedpod, leaf and petal as inspiring materials for superhydrophobicity and antireflective models.

2.1.1Canna Indica seedpod:

The seed pods, which were in green and red colour consists of high aspect ratio cone like microstructures (bumps) as shown in the Figure 2.1(a). These microstructures are imposed by nanostructures which were seen uniformly spread along the bumps and were responsible for superhydrophobic behaviour where water droplets are rolled over the bumps without being trapped in-between the bumps as shown in the Figure 2.1(b).

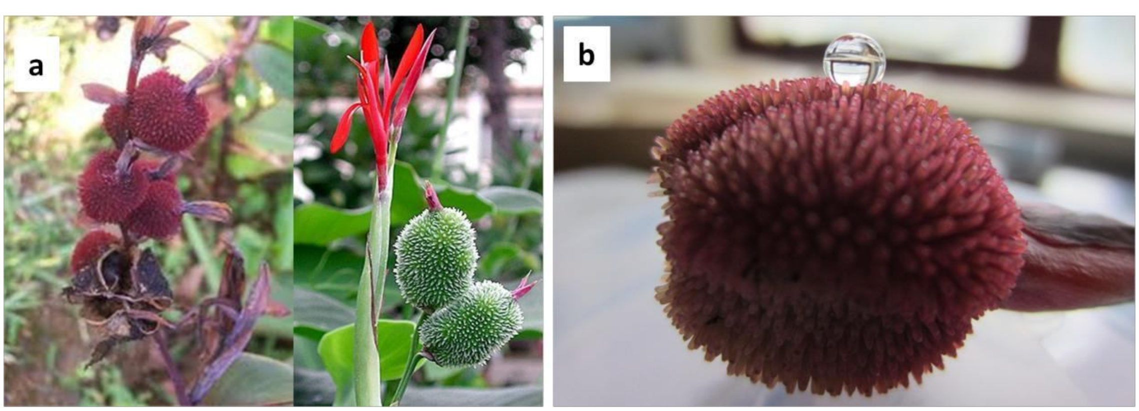

Figure 2.1: (a) Indian canna plant with seedpods [33], (b) Seedpod showing superhydrophobic in nature.

2.1.2 Canna Indica petal:

Like Canna Indica seedpod, Canna Indica flowers can also be available in different colours like yellow, pink, red in nature. In this work we have used red colour Canna Indica flower petal as an antireflective material as shown in the Figure 2.2 (a). We can also see water droplet was freely residing on red colour petal as shown in the Figure 2.2 (b).

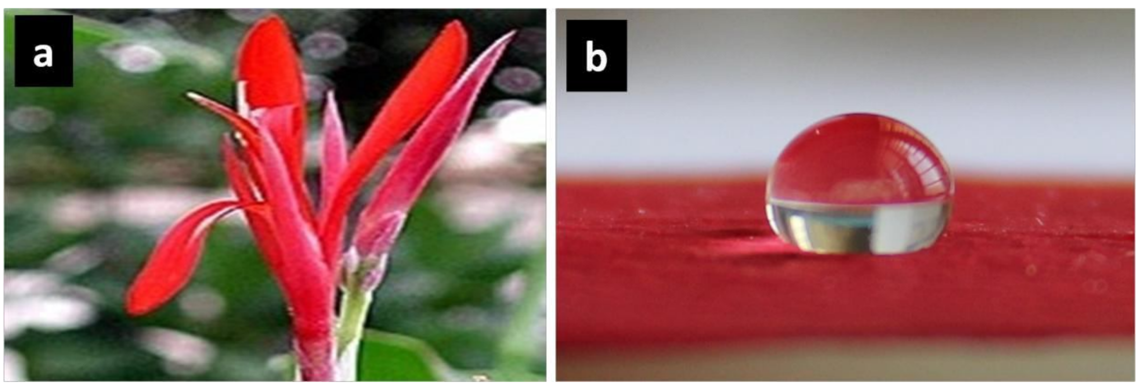

Figure 2.2: (a) Indian canna flower [30], (b) Water droplet residing on flower petal.

2.1.3 Canna Indica leaf:

As mentioned in the section 2.1 Canna Indica plant is also widely grown as garden plant like other garden plants, individual leaf of Canna Indica was clearly shown in the Figure 2.3 (a). We can observe water droplet was freely residing on the leaf as shown in the Figure 2.3 (b). Work on superhydrophobic properties of Canna Indica leaf has been already reported [35].

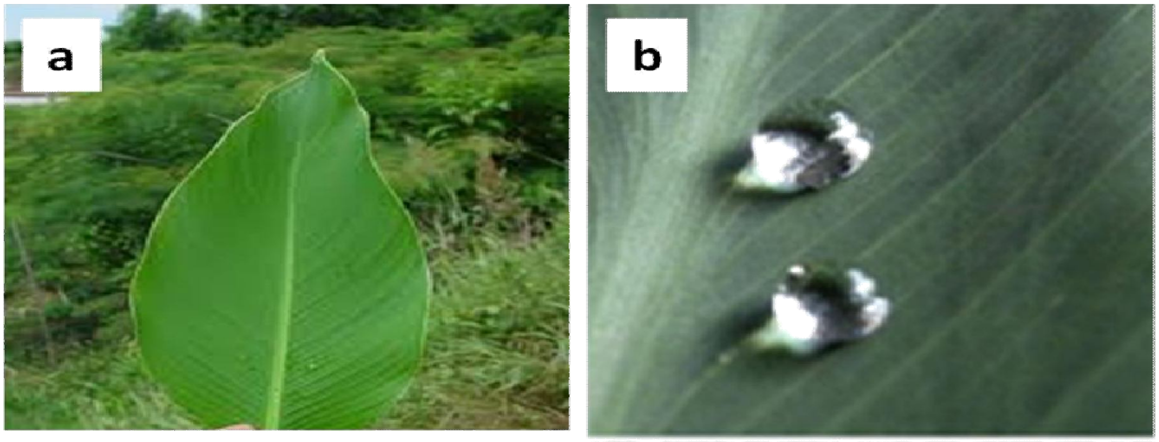

Figure 2.3: (a) Indian canna leaf [34], (b) Water droplet residing on Canna Indica leaf [35].

2.2 Chemicals

Sylgard 184 prepolymer solution (consisting of two part polydimethylsiloxane (PDMS) elastomer and a cross-linking agent) were purchased from Dow corning. Whereas chloroform, resorcinol (99% purity), formaldehyde (37%-41% w/v), potassium carbonate were obtained from (99% purity) Merck India, acetone from Vasco India (99.5%), DI water from AMS enterprises India.

2.3 Replication of hierarchically structured plant surfaces:

The micro and nanostructures of plant surfaces especially leaves and petals are responsible for different properties and functions like wetting properties and optical properties since they have light harvesting organs. The replication techniques used for the fabrication of biomimetics surfaces should be fast and cost efficient. The fabrication of such functional surfaces can be done by using different techniques such as wet and dry etching [36], electron beam lithography [37], hot embossing [38] but these are highly expensive and time consuming techniques. Soft lithography is a technique based on self assembly and moulding. It is a low cost, effective and most convenient method for the fabrication of micro and nanostructures in a precise way. Soft lithography uses soft, organic material (e.g., polymeric material) to generate structures and patterns without the use of light or any other particles [39]. Here we have used replica molding method where we can achieve topographical features. In this method a liquid elastomer is mixed with cross-linker to get a pre-polymer solution, when this pre-polymer solution is poured onto the sample and heated at certain temperature we achieve solid polymer with inverse replica, which can also called as master mold. To this master mold, another polymer is poured to replicate the required features. Here we have also used replica molding technique for bio-mimicking the Canna Indica seedpod, Canna Indica leaf and Canna Indica flower petal by using two polymers such as polydimethylsiloxane (PDMS) and resorcinol-formaldehyde (RF) gel. It is introduced by Pekala [40] as an attractive polymer precursor for glassy carbon.

2.4 Experimental section:

2.4.1 Fabrication of negative PDMS Replica:

The Indian canna seedpod was cut into small piece of 1cm x 1cm length by breadth, and dried at 40° C for 1 hour to remove moisture. The dried seedpod was fixed to a clean glass slide or plane surface with double sided tape as shown in Figure 2.4 (a).Then PDMS solution (10:1 weight ratio of sylgard 184 polymer elastomer and cross-linking agent) poured on to seedpod piece as shown in Figure 2.4 (b) and kept for de-aeration in vacuum desiccator to get rid of bubbles. Later the sample was kept in vacuum oven at 80 °c for 12 hrs for curing (shown in Figure 2.4 (c)). After curing, the PDMS sample is swelled in petridish containing chloroform (shown in Figure 2.4 (d)) for 1 hr. During this treatment, the PDMS sample is detached from the seedpod piece and forms a negative replica of the mold (shown in Figure 2.4 (e)), which was then dried for 1hr at room temperature.

2.4.2 Fabrication of positive RF gel Replica:

To make positive replica from negative replica, we have used RF sol. RF gel is an organic precursor to carbon upon pyrolysis. This RF sol was prepared in aqueous form which contains resorcinol, formaldehyde, water and potassium carbonate [41]. First, 1.27 g resorcinol and 1.3 ml formaldehyde were mixed and stirred together continuously until we get clear solution. In another beaker we took 0.136 gm potassium carbonate and added 5.6 ml of water followed by stirring together until we get clear solution. Finally, these two solutions were mixed and stirred continuously for 15 to 20 min until RF sol was changed to golden yellow colour.

Before pouring the RF sol into the negative replica, the negative PDMS replica was swelled in chloroform for 1 hr or UV treated for 15 min which helps RF sol to wet the pores, since PDMS is hydrophobic in nature [42]. We need to ensure that the sol should be little viscous before pouring into negative PDMS replica to avoid brittleness of positive RF gel. This RF sol was poured to the swelled PDMS replica (shown in Figure 2.4 (f)) and deaerated for 30 min in vacuum desiccator to remove any gas bubbles. Then the sample was kept at room temperature for 12 hrs to undergo gelation. After sol converted into gel, it is peeled off from the negative replica by swelling the PDMS sample in chloroform (shown in Figure 2.4 (g)) for 1hr and allowed for drying at 40° to 50° in hot oven for 12 hrs to avoid breakage (shown in Figure 2.4 (h)). The dried RF replica is removed from oven (as shown in Figure 2.4 (i)) to get the positive replica.

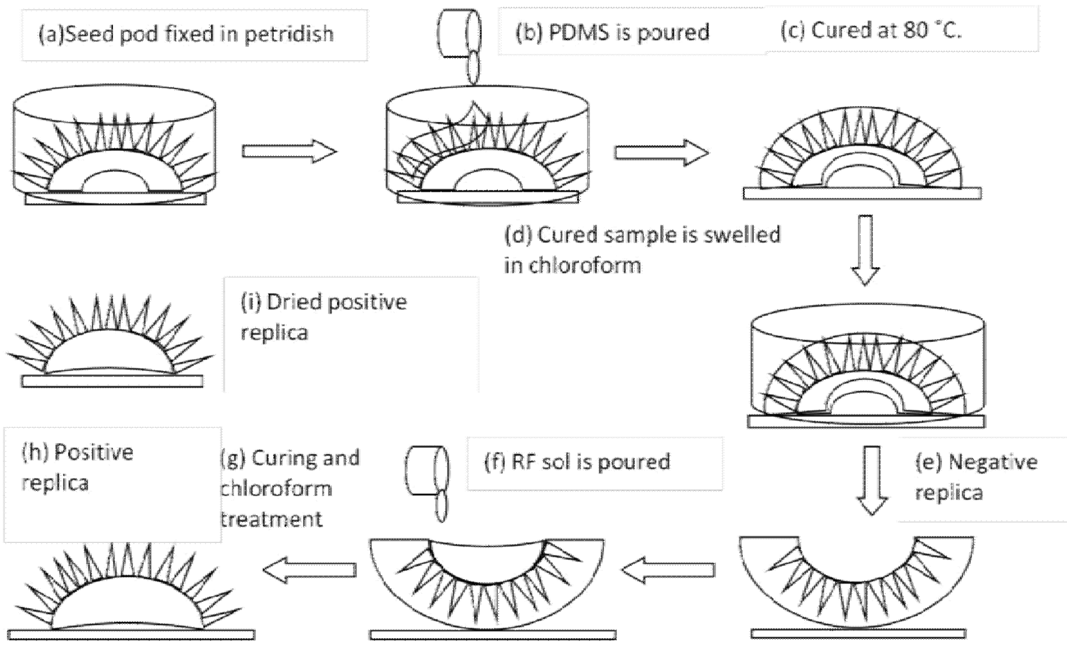

Figure 2.4 (a) First, the seedpod is cut into 1.5 cm x 1.5 cm pieces and pasted on a planar surface, (b) PDMS solution is then poured onto it to create the negative replica, (c) Curing is done at 80°C for 12hrs, (d) PDMS stamp was separated from original seedpod by swelling in chloroform, (e) Negative replica containing holes is created, (f) RF sol is poured to negative PDMS replica containing holes, (g) RF gel was separated from negative PDMS replica by swelling in chloroform,(h) RF gel positive replica was generated, (i) dried positive replica.

2.5 Characterization Equipments:

2.5.1 Scanning Electron Microscope (SEM):

Scanning electron microscope uses an electron beam as a source to scan the samples. Here we have used Hitachi S-3400N SEM. As polymer is a non-conducting material, it was coated with thin layer of gold by using gold sputter unit JEOL fine coat JFC1100E.

2.5.2 Confocal Microscopy:

The Olympus LEXT OLS4000 is a confocal microscope is used to magnify the surface of Indian Canna seedpod. It is capable of taking high resolution 3D images and magnification ranges from 108x –17,280x. It is capable of resolving features 10 nm in size in the z direction (sample height) and 120 nm in the xy plane (sample width and length). A variety of measurements can be performed on 3D images generated by the scope, including step heights, surface profiles, and area etc.

2.5.3 Contact angle:

The wettability of the materials was determined by the static contact angle (CA) measurement. Here we have used VCA optima contact angle system for contact angle measurement with a digital camera to create a magnified profile of droplet. For this purpose, 10µl droplets de-mineralized water was applied to the material by automatic dispenser connected to the system.

2.5.4 UV-VIS Spectroscopy:

For the reflection studies we have used Perkin Elmer Lambda 35 UV-VIS Spectroscopy. When electromagnetic radiation in the UV/Visible wavelength range hits the sample, four outcomes are possible: the radiation is absorbed, transmitted and reflected. In this work we have mainly concentrated on reflectivity. However, with proper equipped and proper accessories, UV/Vis spectrometer can measure the reflected and scattered energy from a sample.

2.5.5 3-D Optical profilometer:

3-D optical profiler (AEP NanoMap-D) is an instrument with large scanning range which allows generating high resolution 2Dand 3D images. It allows for both tip and stage scan modes. Tip scan mode uses piezo drive to move the stylus up to 500x500 micron area and generates high resolution image. Whereas stage scan mode moves the sample stage to generate high resolution image. Here in this work we have used stage scan mode to generate high resolution 2D and 3D images.

Summary:

In this chapter we have discussed about the India canna plant (Canna Indica), experimental technique used to mimic the patterns from India canna plant, main equipments used for characterization, such as SEM, contact angle measurement, and confocal microscopy and UV-VIS spectroscopy.

Chapter 3

Wettability studies

3.1 Canna Seedpod

The Indian canna seedpod with high aspect ratio hierarchical structures was replicated using different polymers like PDMS and RF sol. As mentioned in experimental procedure in section 2.5, the negative replica of the mold can be done in two ways. One, the seed pod is attached to petridish surface; pour the polymer on the top surface of seed pod where bumps are in upward directions. Second, pour the polymer first into petridish and put the seed pod in inverse way i.e. the bumps should face downwards. We need to ensure that the seedpod is fixed properly to the petridish to avoid floating of seed pod in polymer which results an uneven coverage of polymer along the bumps. Sufficient amount of polymer was poured above the bumps to avoid leakage of RF gel, during swelling of cured polymer; chloroform will make holes to the polymer if polymer thickness is very less. Deareation was done to samples before curing, to remove any trap air bubbles in between the bumps.

3.1.1 Surface morphology:

Plant surfaces exhibits a large diversity of hierarchical structures with different functions. Hierarchy in surfaces textures leads to water repellent and self-cleaning process. The hierarchical patterns seen on different leaves like lotus leaf, rice life and taro leaf are limited to low aspect ratio structures, whereas the Indian Canna seedpod, which is used in this work shows high aspect ratio bumps like structures each around 3 to 5 mm height to which microstructures are imposed by nanostructures. Surface morphology of biomimicked structure were observed using Hitachi S-3400N SEM as shown in the Figure 3.1. SEM images of original seedpod in the Figure 3.1 (a1, b1, c1, and d1) showing hierarchical patterns on the tapered bumps show in Figure 3.1 (a1), (b1), in Figure 3.1 (c1) and (d1) at different magnifications shows micro and nanostructures 20μm and 0.4μm. SEM analysis has also done for PDMS negative replica as shown in the Figure 3.1 (a2, b2, c2, d2). At lower magnifications we can see small holes like structures as shown in Figure 3.1 (a2), (b2) and at higher magnifications we can observe small micro/nano structures inside the holes of 24μm, 0.3μm as shown in Figure 3.1 (c2), (d2). Finally, SEM analysis was also done for RF gel positive replica as shown in Figure 3.1 (a3, b3, c3, d3), having tapered structures similar to original seedpod, also having some hierarchical patterns on the tapered bumps shown in Figure 3.1 (a3), (b3), and we can notice some micro/nanostructures 27μm, 0.6μm in scale at higher magnifications as shown in Figure 3.1 (c3), (d3).

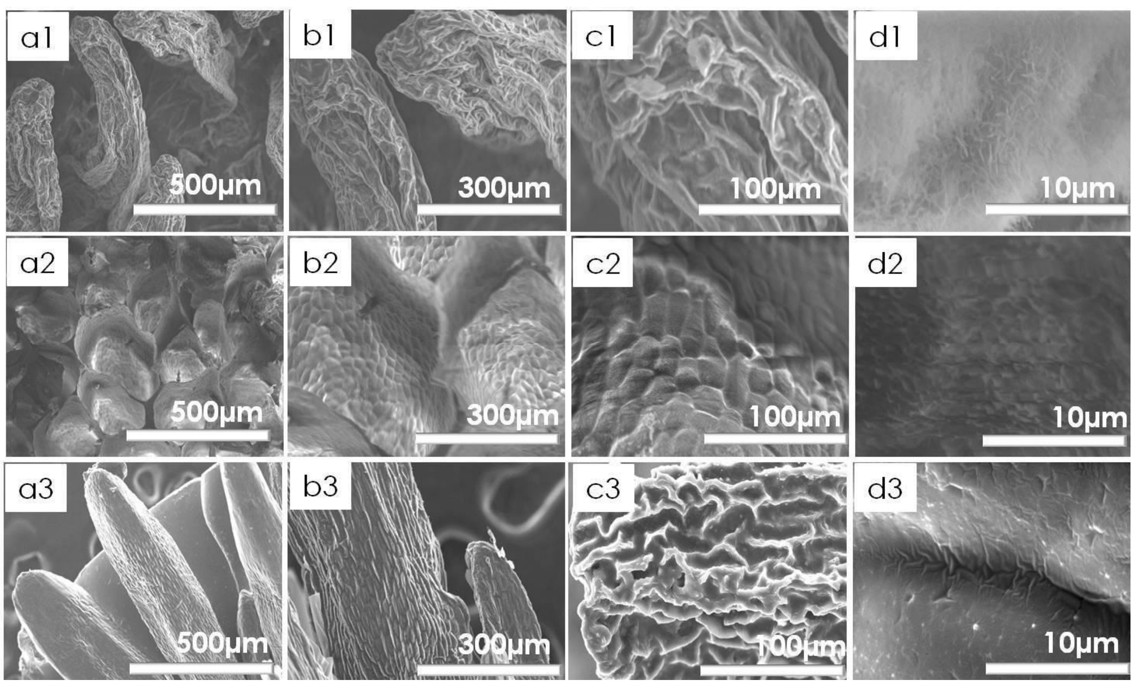

Figure 3.1: SEM images of original Indian canna seed pod (a1-d1), negative PDMS replica (a2-d2), and RF gel positive replica (a3-d3) at various magnifications.

3.1.2 Confocal Microscopy Images:

The high aspect ratio structures of Indian canna seedpod were observed by using Olympus lext confocal microscope to measure length and width of each bump as shown in the Figure 3.2. An individual bump of 434.73µm in height and 137.56µm in width having tapered like structure is shown in Figure 3.2 (a). In Figure 3.2 (b) we can see group of bumps having different height and width having aspect ratio of 3:1. Profile measurement images of the bumps can be seen in Figure 3.2 (c), (d).

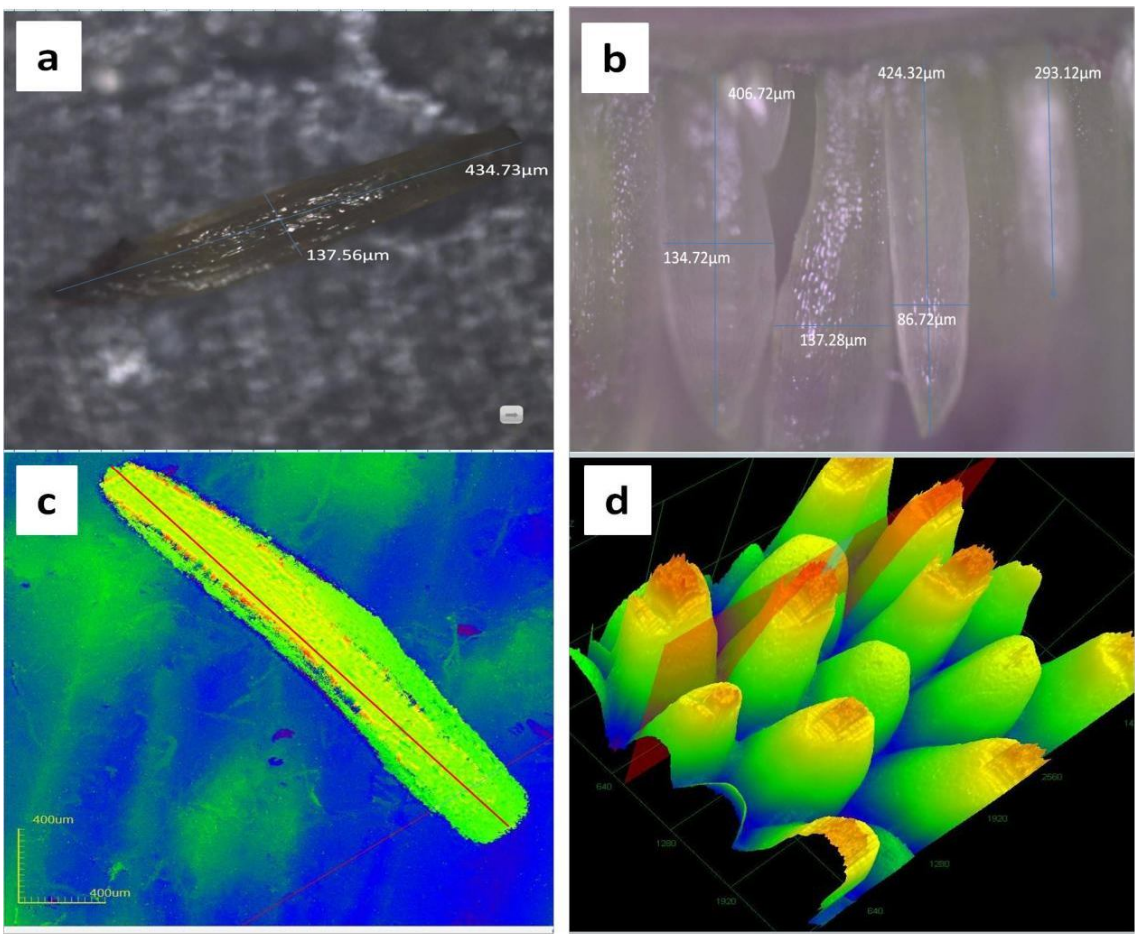

Figure 3.2: Confocal microscopic images of (a) Height and width of individual bump, (b) Height and width of different bumps, (c) Profile measurement image of individual bump, (d) Profile measurement image of small piece of seedpod consisting bumps.

3.1.3 Water contact angle measurement:

As mentioned in the section 1.2, surfaces which shows contact angle greater than 90° are termed as hydrophobic and while more specifically the surfaces with contact angle above

150° are termed as superhydrophobic. To check the wettability characteristics, water contact angle was measured by goniometer on original Indian canna seedpod, negative PDMS as well as high aspect ratio hierarchical RF gel replica. These results were summarized in Figure 3.3 Digital camera images of water droplet residing on the surface of original seed pod (Figure.3.3 (a1)), negative PDMS replica (Figure.3.3 (b1)), and RF gel positive replica (Figure.3.3 (c1)) are shown. By using goniometer, original seed pod shows water contact angle of $151^\circ \pm 1.63^\circ$ as shown in Figure 3.3 (a2), while negative PDMS replica having holes water contact angle $136^\circ \pm 1.63^\circ$ as shown in Figure 3.3 (b2)). Interestingly, it was observed RF gel replica with high aspect ratio hierarchical patterns show superhydrophobic behaviour with water contact angle $155^\circ \pm 1.14^\circ$ as shown in Figure 3.3 (c2).

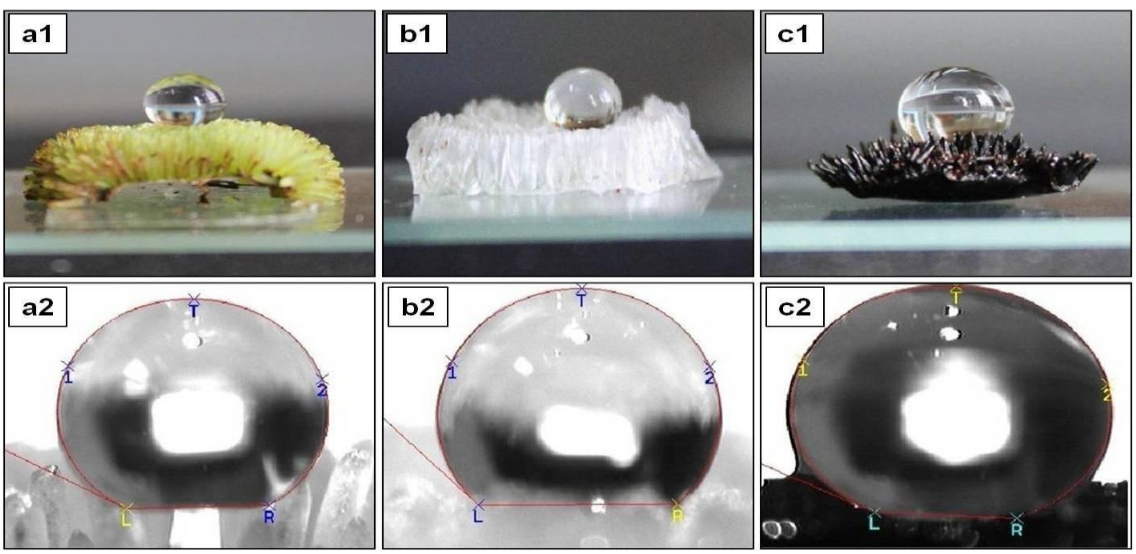

Figure 3.3: Digital camera images showing the water droplet on (a1) original Indian canna seedpod, (b1) negative PDMS replica, and (c1) RF gel replica. Water droplet Images on (a2)

original Indian canna seed pod, (b2) negative PDMS replica, (c2) RF gel replica using contact angle goniometer.

3.2 Canna Indica Leaf:

The Canna indica leaf having low aspect ratio micro-nanostructures was also responsible of superhydrophobic behaviour. The replication of canna indica leaf was done in similar way as for seedpod discussed in the experimental section 2.5.1 by using two polymers PDMS and RF. Before pouring the PDMS pre polymer, we must ensure that the canna leaf properly attached to the surface by using double sided tape to avoid rolling. PDMS replica was UV exposed for 20 min, before pouring the RF sol to the negative PDMS replica to create low surfaces energy and thus allowing complete wetting the leaf replica in PDMS.

3.2.1 Surface morphology:

Surface morphology of original canna indica leaf and biomimicked structures were observed using SEM as shown in the Figure 3.4 SEM images of original canna indica leaf showing micro structured patterns are shown in Figure 3.4 (a1), (b1), (c1) and (d1). At higher magnifications we can observe micro/nanostructures features of about 23µm/600nm as shown in Figure 3.4 (c1) and (d1). SEM analysis was also done for PDMS negative replica where we can see small holes like structures as shown in Figure 3.4 (a2), (b2) and (c2). At higher magnifications we can observe holes of about 17um as shown in Figure 3.4 (c2). Finally, SEM analysis has also done for RF gel positive replica as shown in Figure 3.4 (a3, b3, c3, d3), here also we can observe some micro structured features of about 26 µm as shown in Figure 3.4 (c3).

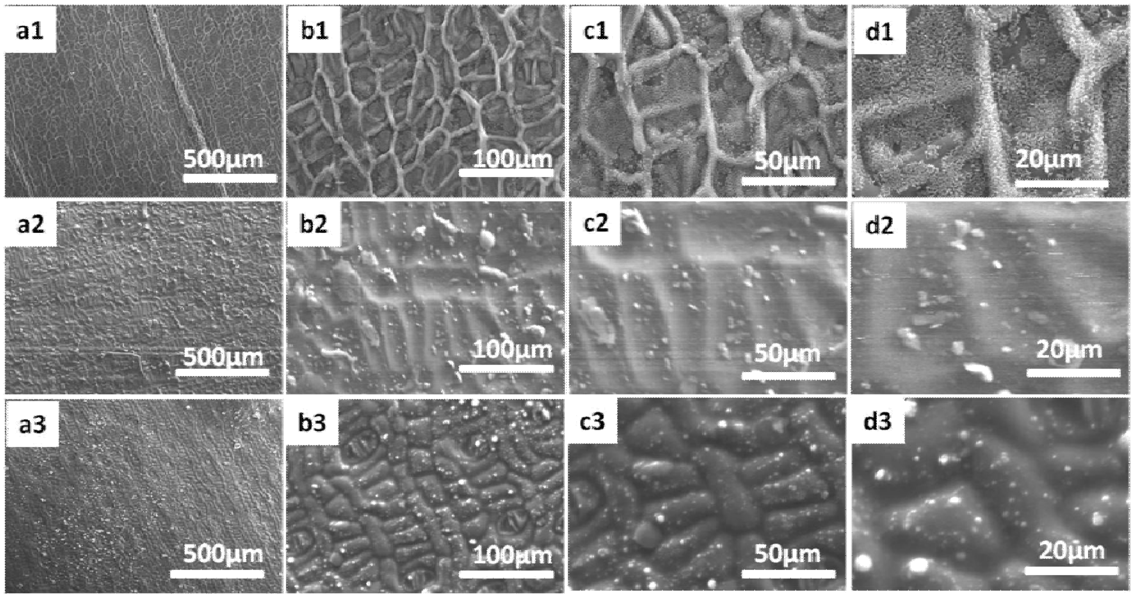

Figure 3.4: SEM images of original Indian canna leaf (a1-d1), negative PDMS replica (a2-d2), RF gel positive replica (a3-d3) at various magnifications.

3.3 Canna Indica petal:

The canna indica flower petal which is a transform of seedpod having low aspect ratio cone like bumps of 1 3µm to 0.3 µm also shows superhydrophobic in nature. The experimental details for replication of petal and its biomimicked structures are same as reported in earlier section 2.5.

3.3.1 Surface morphology:

Surface morphology of the original petal and biomimicked structures were observed by using SEM as shown in the Figure (3.5). SEM images of original canna petal were shown in the Figure 3.5 (a1-d1) at different magnification. SEM images of negative PDMS replica of petal containing holes as shown in the Figure 3.5 (a2-d2). At higher magnification we can observe holes of about 16µm to 18µm as shown in Figure 3.5 (c2). SEM images of positive RF gel of canna petal were shown in Figure 3.5 (a3-d3). We can observe small tiny bumps like features as shown in Figure 3.5 (b3) and at still higher magnification we can see individual bumps of 10µm to 12um features as shown clearly in the Figure 3.5 (c3) and (d3).

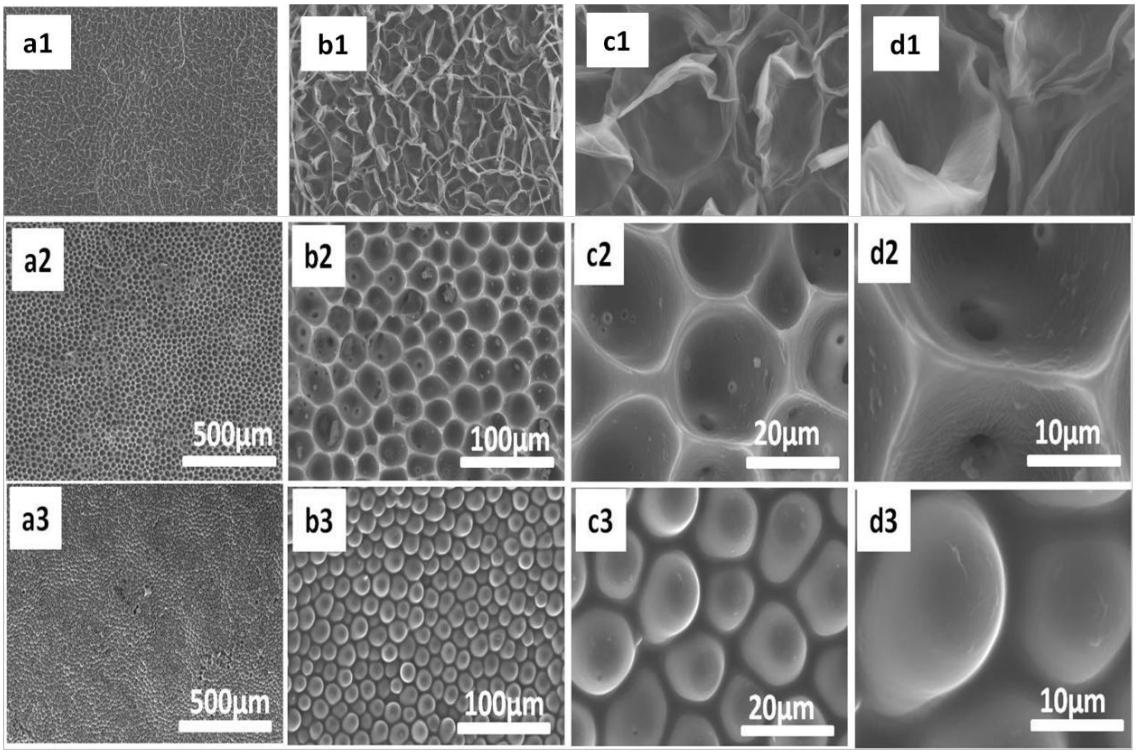

Figure 3.5: SEM images of original Indian canna petal (a1-d1), negative PDMS petal replica (a2-d2), RF gel positive petal replica (a3-d3) at various magnifications.

3.3.2 Water Contact angle measurement:

To check the wettability characteristics, water contact angle was measured by using goniometer, on original flower petal, negative PDMS replica of petal and positive RF gel replica of petal as shown in Figure 3.6. Figure 3.6 (a1-c1) shows digital camera images of water residing on original petal (a1), negative PDMS replica (b1) and positive RF gel replica of petal (c1). While Figure 3.6 (a2-c2) shows water contact angle on original petal of $137^{\circ} \pm 1.29^{\circ}$ (a2), negative PDMS replica of petal of $152^{\circ} \pm 1.82^{\circ}$ (b2) and positive RF gel replica petal of $140^\circ \pm 1.63^\circ$ (c2) by using goniometer. Interestingly we found negative PDMS replica show greater angle compared to original petal and positive RF gel replica.

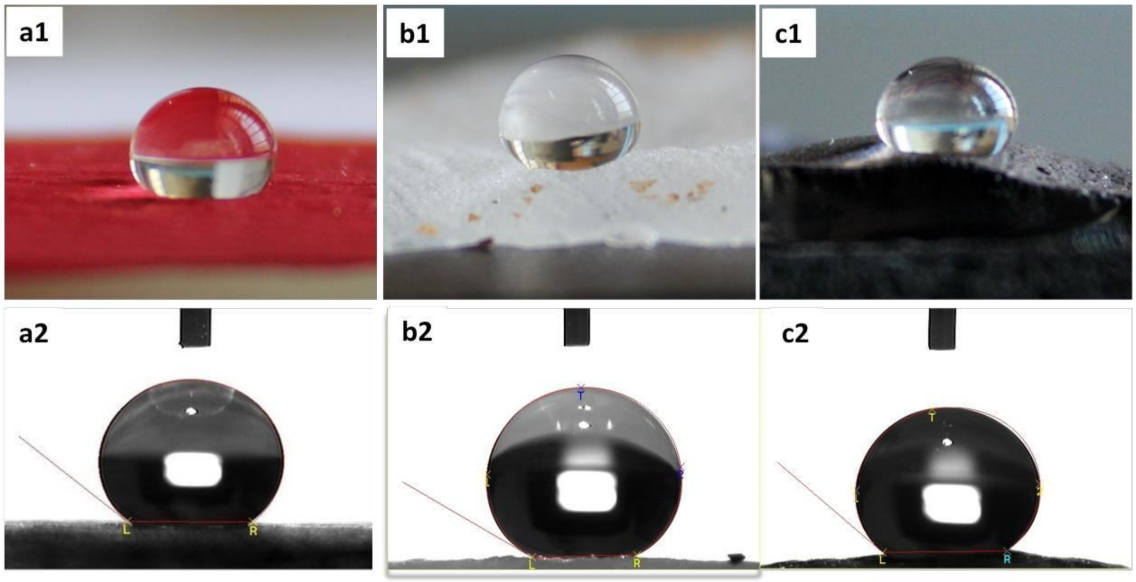

Figure 3.6: Digital camera images showing the water droplet on (a1) original Indian canna petal, (b1) negative PDMS replica, and (c1) RF gel replica. Water droplet images on (a2) original Indian canna petal, (b2) negative PDMS replica, (c2) RF gel replica using contact angle goniometer.

Summary:

To summarise this chapter, we have done wettability studies for Canna Indica seedpod, Canna Indica petal and their biomimicked surfaces. We have observed that the replicated (biomimicked) surfaces shows high contact angle than the original surfaces.

Chapter 4

Antireflective studies

4.1 Roughness measurements:

As discussed in the section 1.4, petal surfaces having convexly shape epidermal cells shows less reflection by occurring multiple reflection between the bumps. For reflection and transmission measurements we have done the roughness measurement analysis for the Canna Indica petal, canna indica leaf and their biomimicked surfaces of 5cm x 5cm area samples by using AEP 3D optical profilometer (NanoMap-D) to generate high resolution 3D and 2D images as shown in the Figure 4.1 (a) and (b). While 2D images of original Canna Indica petal and positive RF petal replica were shown in the Figure 4.1 (a1) and (b1). We have also done 3D analysis for negative PDMS leaf replica having gaps in between the rough surface as shown in the Figure 4.1(c) and 2D analysis of positive RF leaf replica. By using same optical profilometer we have also checked the different output values like Sa (roughness average roughness), Sq (root mean square roughness), Sp (Maximum peak height) and Sv (reduced value depth) as shown in the Table 4.1. If we observe the roughness average roughness of original Canna Indica leaf and positive RF leaf replica having almost near values 69.2 nm and 52.1 nm as shown in the Table 4.1. Similarly we can observe for Canna Indica petal and positive RF petal replica having almost similar values 13.5 µm and 13.2 µm as shown in the Table 4.1. We can also observe almost similar values for the other profile measurements as shown in Table 4.1.

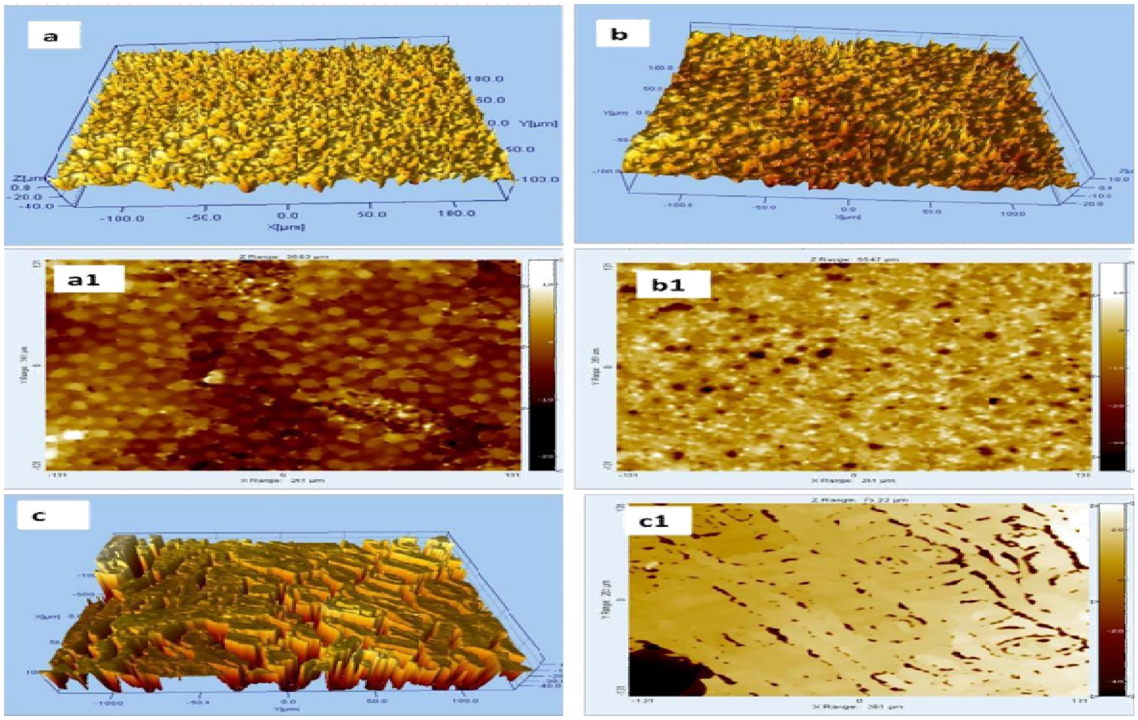

Figure 4.1: Roughness analysis of high resolution 3D images (a) original Canna Indica petal, (b) positive RF petal replica, (c) Negative PDMS Canna Indica leaf replica, and high resolution 2D images (a1) original Canna Indica petal, (b1) positive RF petal replica and (c1) positive RF leaf replica.

Table 4.1 Roughness measurement profiles of Canna indica leaf, Canna indica petal and their biomicked surfaces.

Output values	Original leaf	Negative PDMS leaf	Positive RF leaf	Original petal	Negative PDMS petal	Positive RF petal
Sa, average roughness	69.2 nm	68.9 nm	52.1 nm	13.3 µm	14.5 µm	13.4 µm
Sq, RMS roughness	69.8 nm	83.8 nm	67.2 nm	14.2 µm	18.4 µm	15.3 µm
Sp, Maximum peak height	87.4 nm	171.5 nm	91.7 nm	16.8 µm	22.5 µm	20.9 µm

4.2 Reflection studies:

Reflection studies were analysed for Canna Indica leaf and Canna Indica petal by using Perkin Elmer Lambda-35 UV-VIS spectroscopy. The instrument settings were follows.

Scan Range Start	900	nm
Scan Range End	400	nm
Scan Speed	480	nm/min
Data Interval	1	nm
Cycle Count	1	
Cycle Time	1	s
Ordinate Type	%R	
Slit Width	2	nm
UV Lamp On	Yes	
Visible Lamp On	Yes	
Lamp Change-over Wavelength	326	nm

4.2.1 Canna Indica petal:

The plant organs such as leaves and petals are light harvesting organs as they absorb light with the help of photosynthetic process. Generally, plant processes electromagnetic radiation in the blue (400-480nm) spectral range and yellow (550-770nm) spectral range. These wavelengths are absorbed by photosynthetic reaction material called chlorophyll. By inspiring from this, scientific investigation has done to explore the optical properties [43], [44]. However surface textures of leaves and petals also plays important role in absorbance, transmission and reflection of light. In this work we have used Canna Indica petal and Canna Indica leaf which are having hierarchical structures on their surfaces. To check how much of light is reflected from the original petal surface and replicated surfaces, reflection studies were done for original canna indica petal, bio-mimicked surfaces (negative PDMS petal replica and positive RF gel petal replica), plain PDMS and plain RF gel of 5cm x 5cm area samples by using UV-VIS spectroscopy of wavelength ranges from 400nm – 800nm (X-axis), which is visible wavelength at 30° incidence angle and %Reflection in Y-axis as shown in the Figure 4.2. The curve at which is in light blue colour indicates the plain RF gel surface shows reflection of 0.68% which is in Y -axis, where as the curve which is in green colour indicates the structured RF gel sample having bumps (positive RF petal replica) shows 0.02% significant decrease in reflection compared to plain RF gel surface. The curve which is in light purple colour indicates plain PDMS surface shows reflection of 0.29%, where as the curve which is in dark blue colour indicates structured PDMS surface having holes (negative PDMS petal replica) shows 0.04% significant decrease in reflection compared to the plain PDMS surface. The curve which is in light red colour indicates original canna indica petal shows reflection of 0.03% up to 510nm and there is gradual increase in reflection, since the pigments in the petal absorb the blue spectral region (400nm to 480nm) green spectral region (480nm to 550nm) and reflects the yellow and red region (550nm to 700nm). We can observe that biomimicked petal surfaces show less reflection than the standard surfaces.

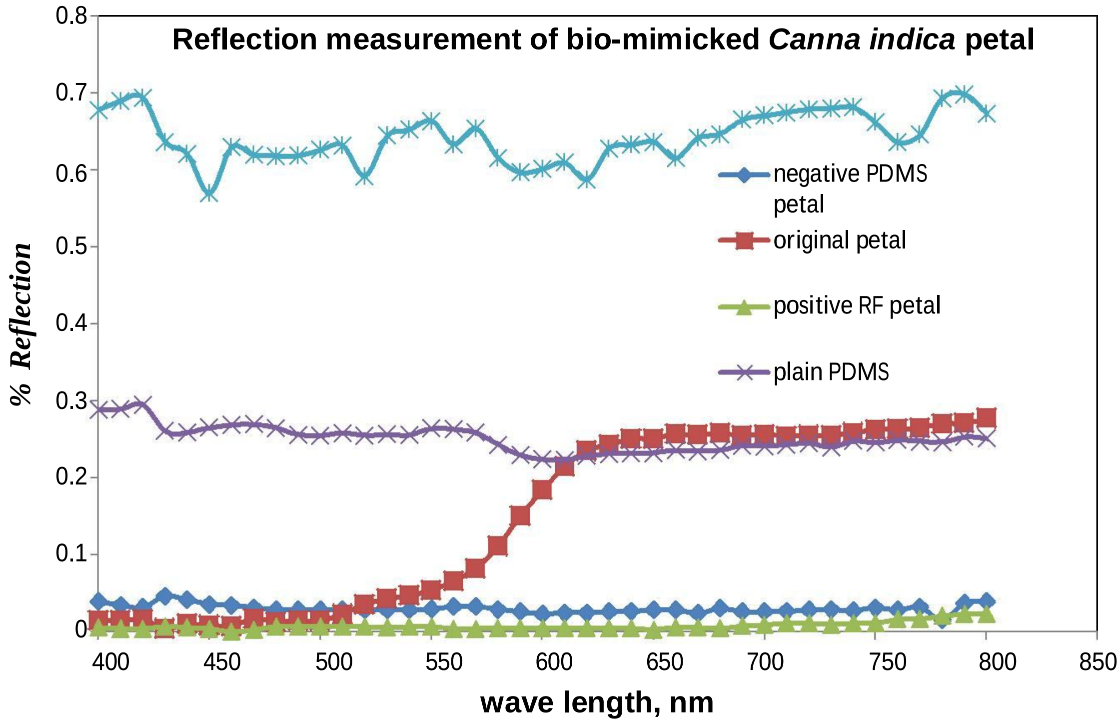

Figure 4.2: Reflection measurement of original canna indica petal, plain PDMS, plain RF, structured PDMS surface (negative PDMS petal replica) and structured RF surface (positive RF gel petal replica) at 30 deg angle wavelengths ranging from 400nm-800nm.

4.2.2 Canna Indica leaf:

Reflection studies was also done for original canna indica leaf, bio-mimicked surfaces (negative PDMS leaf replica and positive RF gel leaf replica), plain PDMS and plain RF gel by using UV-VIS spectroscopy of wavelength ranges from 400nm – 800nm (X-axis), which is visible wavelength at 30° angle and % Reflection in Y- axis as shown in the Figure (4.3). The curve at which is in light blue colour indicates the plain RF gel surface shows reflection of 0.68% which is in Y -axis, where as the cure which is in green colour indicates the structured RF gel surface (positive RF leaf replica) shows 0.02% significant decrease in reflection compared to plain RF gel surface. The curve which is in light purple colour indicates plain PDMS surface shows reflection of 0.29%, where as the curve which is in dark blue colour indicates structured PDMS surface (negative PDMS leaf replica) shows 0.1% significant decrease in reflection compared to the plain PDMS surface. The curve which is in light red colour indicates original canna indica leaf shows low reflection of 0.03% up to 500nm and there is sudden increase in reflection from 0.03% to 0.07% up to 590nm and again decrease of reflection of 0.03% up to 700nm, since the leaf pigments absorb the blue spectral region (400nm to 480nm), yellow through red region (550nm to 700nm) and reflects green spectral region (480nm to 550nm). Like petal biomimicked surfaces, we can also observe that leaf biomimcked surfaces show less reflection than the standard surfaces.

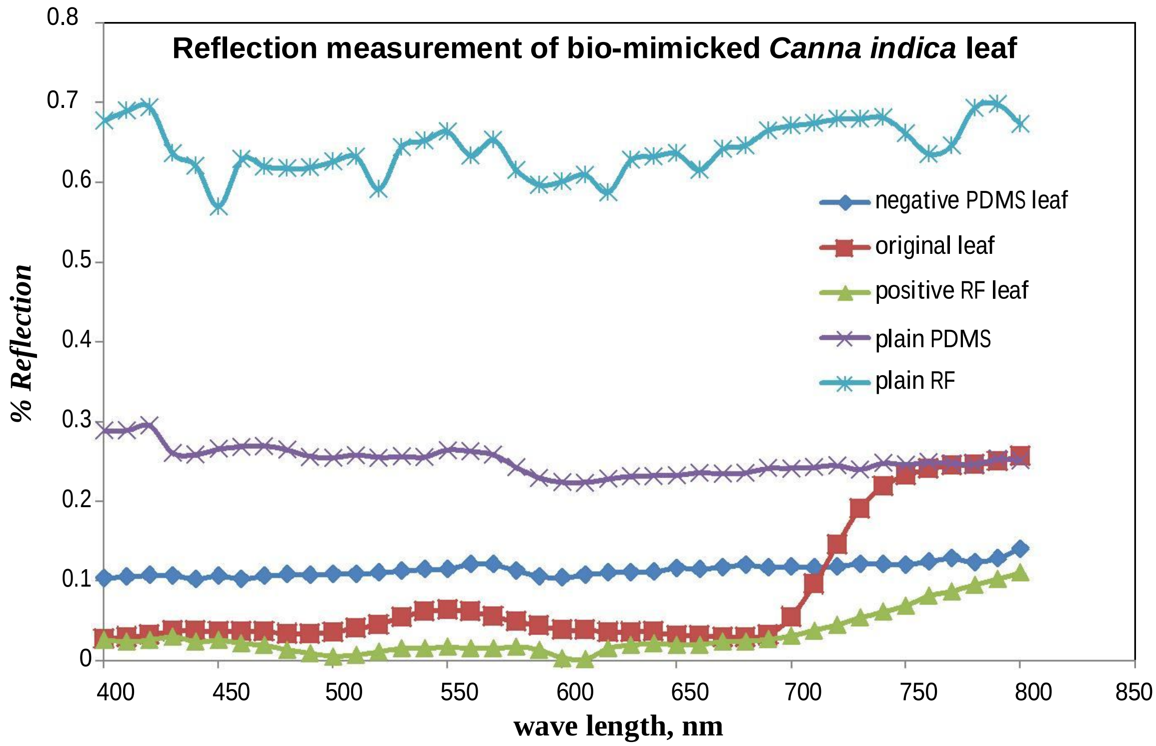

Figure 4.3: Reflection measurement was for original canna indica leaf, plain PDMS surface, structured PDMS surface (negative PDMS leaf replica) and structured RF gel surface (positive RF gel leaf replica) at 30 deg angle wave length ranging from 400nm-900nm.

4.3 Variable angle reflectance studies:

Variable angle reflection studies were analysed for canna indica leaf and canna indica petal by using Perkin Elmer Lambda-35 UV-VIS spectroscopy. The instrument settings are as follows.

Scan Range Start	700	nm
Scan Range End	700	nm
Scan Speed	480	nm/min
Data Interval	1	nm
Cycle Count	1	
Cycle Time	1	s
Ordinate Type	%R	
Slit Width	2	nm
UV Lamp On	Yes	
Visible Lamp On	Yes	
Lamp Change-over Wavelength	326	nm

Suppressing of reflectance from any surface can be achieved by single layer thin film antireflective coating however that is limited to certain angle of incidence of light. As the day long from sun rise to sun set, solar radiations will be emitted by the sun at different angle of incidence. To overcome these problem multi layer antireflective coatings were applied to the surfaces by replacing single layer antireflective coatings. However, these multi layer antireflective coating are also limited to adhesion problem and high cost. This multi layer antireflective coating can be replaced by Sub-wavelength structures as discussed in section

1.4. Here we have used canna indica petal, leaf and their bio-mimicked surfaces as antireflective materials which are having sub-wavelength structures.

4.3.1 Canna Indica petal:

To check how much of light is reflected from the original petal surface and replicated surfaces by varying angle of incidence of light and keeping wavelength constant. Variable angle reflection studies were done for original canna indica petal, bio-mimicked surfaces of 5mm thickness (negative PDMS petal replica and positive RF gel petal replica), plain PDMS surface and plain RF gel surface of 5mm thickness by using UV-VIS spectroscopy of keeping wavelength constant 700nm and varying the light incident angle from 30° to 70° (X-axis) and % Reflection in Y-axis as shown in the Figure 4.4. The curve green indicates the plain RF surface shows reflection of 0.8% at 30° incident angle of light and gradual increase in reflection up to 4.3% at 60° incident angle of light and sudden decrease in reflection reaches almost 0% at 70° incident angle of light. The curve which is in light blue colour indicates the structured RF surface (positive RF petal replica) shows reflection of almost 0% at all angle of incidence of light. The curve which is light red colour indicates plain PDMS surface shows reflection of 0.3% at 30° angle of incidence of light and gradually decreases almost 0% of reflection at 50° angle of incidence of light; from there it is gradually increases and shows 3.7% reflection at 70° angle of incidence of light. Whereas the purple curve indicates structured PDMS surface, which shows almost reflection of 0% at all angle of incidence of light. The curve which is in blue colour indicates original petal shows reflection of 0.2% at all angle of incidence of light. From the results we can observe irrespective of angle of incidence of light the biomimicked petal surfaces shows less reflection compared to the standard surfaces.

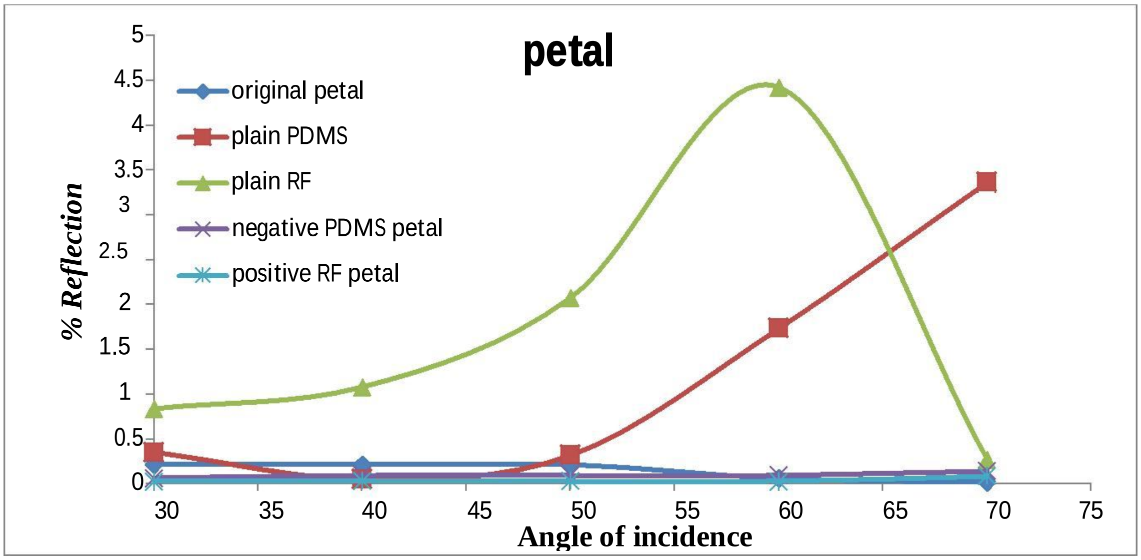

Figure 4.4 Variable angle reflectance measurements of original Canna Indica petal and their biomimicked surfaces. Irrespective to the angle of incidence of light petal biomimicked surfaces shows low reflection compared to the standard surfaces.

4.3.2 Canna Indica leaf:

Similarly, we have also done variable angle reflectance of Canna Indica leaf and their biomimicked structures, plain PDMS and plain RF gel by using UV-VIS spectroscopy of keeping wavelength constant 700nm and vary the angle from 30° to 70° (X-axis) and % Reflection in Y-axis and as shown in the Figure 4.5. The curve purple indicates the plain RF surface shows reflection of 0.8% at 30° incident angle of light and gradual increase in reflection up to 4.3% at 60° incident angle of light and sudden decrease in reflection reaches almost 0% at 70° incident angle of light. The curve which is in light blue colour indicates the structured RF surface (positive RF leaf replica) shows reflection of almost 0% from 30° to 50° angle of incidence of light and there is a gradual increase of reflection of about 0.3% at 70° angle of incidence of light . The curve which is light green colour indicates plain PDMS surface shows reflection of 0.3% at 30° angle of incidence of light and gradually decreases almost 0% of reflection at 50° angle of incidence of light; from there it is gradually increases and shows 3.7% reflection at 70° angle of incidence of light. Whereas the curve which is in light red in colour indicates structured PDMS sample (negative PDMS leaf replica), which

shows almost reflection of 0.2% from 30° to 40° angle of incidence of light and there is gradual increase of reflection and reaches 0.7% at 70° angle of incidence of light. The curve which is in blue colour indicates original leaf shows reflection of 0.2% from 30° to 60° angle of incidence of light and increased to 0.3 % reflection at 70° angle of incidence of light. Like petal we can also observe that biomimicked leaf surfaces show less reflection than the standard surfaces.

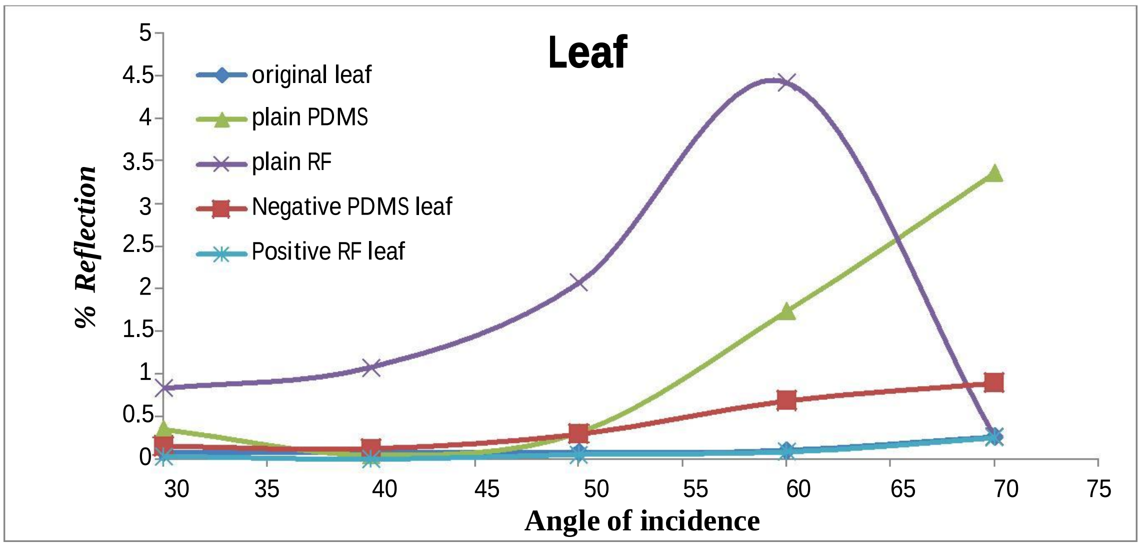

Figure 4.5: Variable angle reflectance measurement of original Canna Indica leaf and their biomimicked surfaces Irrespective to the angle of incidence of light leaf biomimcked surfaces shows low reflection than the standard surfaces.

4.4 Transmission studies:

Apart from reflection, transmission of light passing into the medium also plays important role in fabricating antireflective surfaces. So in this work we have also done transmission studies for canna indica leaf, canna indica petal and their biomimicked surfaces by using Perkin Elmer Lambda-35 UV-VIS spectroscopy. The instrument setting was as follows.

Scan Range Start	800	nm
Scan Range End	400	nm
Scan Speed	480	nm/min
Data Interval	1	nm
Cycle Count	1	
Cycle Time	1	S
Ordinate Type	%T	
Slit Width	2	nm
UV Lamp On	Yes	
Visible Lamp On	Yes	
Lamp Change-over Wavelength	326	nm

4.4.1 Canna Indica petal:

Transmission measurements were done for the canna indica petal and their biomimicked structures at normal angle of incidence of light wavelength ranging from 400nm-800nm (X-axis) and %T in Y-axis as shown in the Figure 4.6. The curve which is in blue colour indicates the plain PDMS surface shows transmission of about 68% to 75% wavelength ranges from 400 nm to 800 nm, where as the curve which is light green in colour indicates the structured PDMS (negative PDMS petal replica) surface which shows a significant decrease in transmission of about 4% wavelength ranges from 400 nm to 800 nm. The curve which is in light blue colour indicates the plain RF surface shows transmission of 0.1 % wavelength ranges from 400 nm to 780 nm and there is a sudden rise of 0.32% up to 800nm, where as the curve which is in dark orange colour indicates structured RF (positive RF petal replica) surface shows transmission almost 0%. We have also done transmission measurement for original petal which is the yellow curve shows almost 0% transmission wavelength ranges from 400 nm to 680 nm and there is a sudden rise of transmission at 680 nm, which reaches 0.3 % transmission at 800nm.

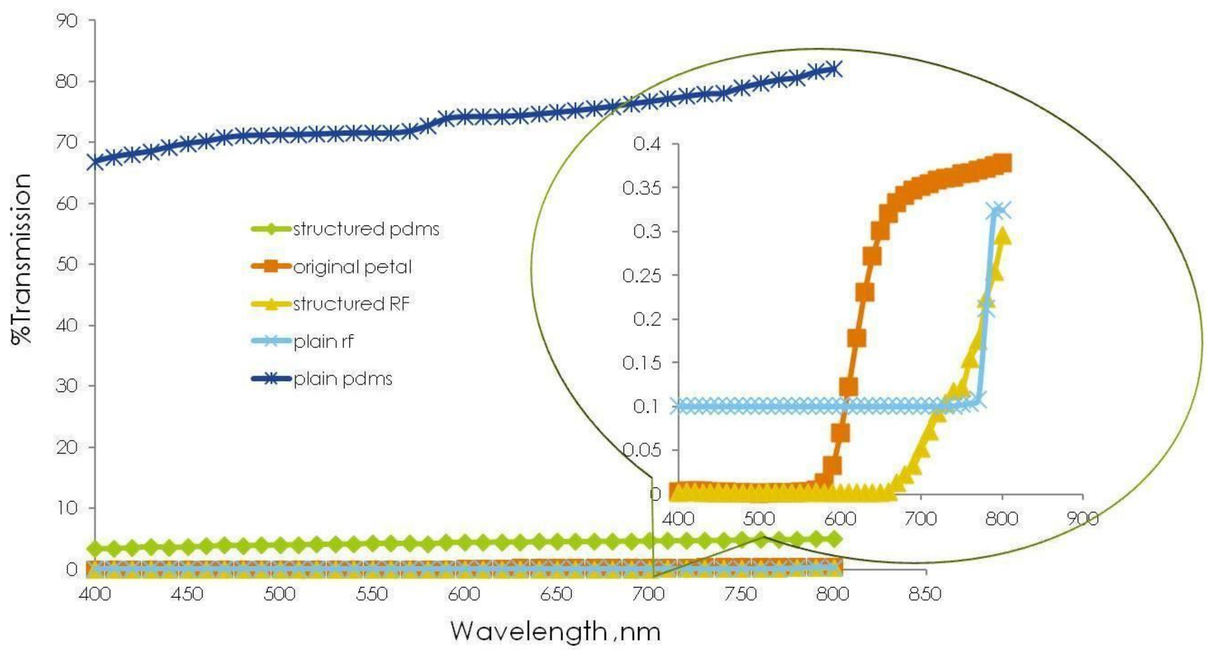

Figure 4.6: Transmission measurement of original canna indica petal and its biomimicked surface.

4.4.2 Canna Indica leaf:

Transmission studies were also done for canna indica leaf and its biomimicked samples at normal angle of incidence of light wavelength ranging from 400nm-800nm (X-axis) and %T in Y-axis as shown in the Figure 4.7. The curve which is in light blue colour indicates the plain PDMS surface shows transmission of about 68% to 75% wavelength ranges from 400 nm to 800 nm, where as the curve which is dark blue colour indicates the structured PDMS (negative PDMS leaf replica) surface which shows a significant decrease in transmission of about 19% wavelength ranges from 400 nm to 800 nm. The curve which is in dark orange colour indicates the plain RF surface shows transmission of 0.1% wavelength ranges from 400 nm to 780 nm and there is a sudden rise of 0.32% up to 800 nm, , where as the curve which is in yellow colour indicates structured RF (positive RF leaf replica) surface shows transmission almost 0%. We have also done transmission measurement for original leaf which is the light green curve shows 0.14% transmission wavelength ranges from 400nm to 680 nm and there is a sudden rise of transmission at 680nm, which reaches 0.3 % transmission at 800 nm.

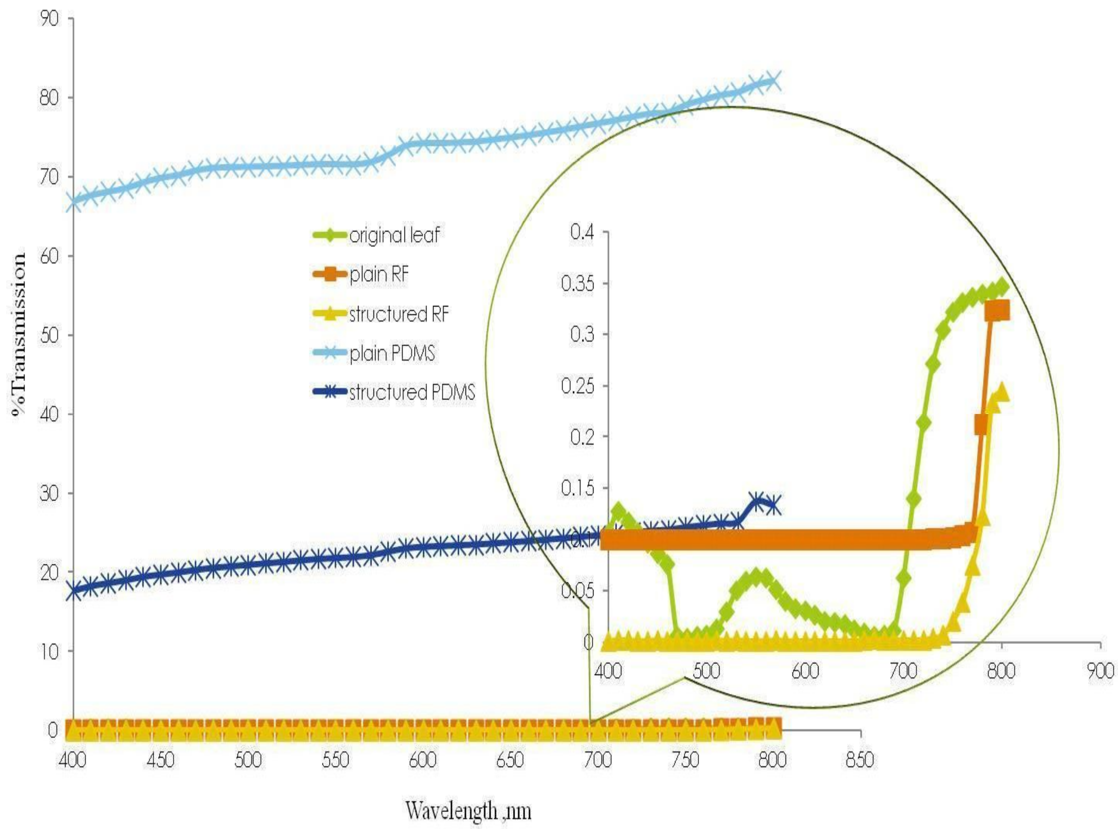

Figure 4.7: Transmission measurement of original canna indica leaf and its biomimicked surfaces.

Summary: In this chapter we discussed about roughness measurements, anti-reflection studies of biomimicked surfaces by fixing angle at various wavelengths and also fixing wavelength at various angles which shows a significant decrease in reflection compared to the standard surfaces. We have also done transmission studies for the same canna indica petal, leaf and their biomimicked surfaces.

Conclusions

In this work, we studied the super hydrophobic nature of India Canna plant. We have depicted a robust method to mimic Indian Canna seed pod, leaf and petal. In case of seedpod, it is the high aspect ratio multiscale structures that cause the superhydrophobicity. However interestingly in case of petal, it is low aspect ratio bump like structures for similar behaviour. We mimicked these structural patterns into a number of polymers like PDMS and an organic (resorcinol formaldehyde) gel and found that these biomimicked polymer surfaces also exhibit superhydrophobic property. Superhydrophobic nature of the original seedpod with high aspect ratio and hierarchical patterns having much larger surface area was not only preserved but also slightly improved in the RF gel replica. Since RF gel is a precursor to carbon, we can also derived superhydrophobic carbon surfaces upon pyrolysis. The petal and leaf biomimicked polymer surfaces with multiscale surface patterns have also been studied for their antireflective properties with an inspiration from the moth eye structure as well as light trapping plant surfaces. The facile fabrication of superhydrophobic as well as antireflective polymer surfaces by a low cost and simple biomimicking route opens the possibilities of using such surfaces for a wide variety of engineering applications including energy storage devices.

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